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<p>(21) International Application Number: PCT/SE99/01291</p> <p>(22) International Filing Date: 19 July 1999 (19.07.99)</p> <p>(30) Priority Data: 9802676-8 6 August 1998 (06.08.98) SE</p> <p>(71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; P.O. Box 9300, NL-6800 SB Arnhem (NL).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): KARLSON, Leif [SE/SE]; Ejdergatan 10, S-444 55 Stenungsund (SE).</p> <p>(74) Agent: ANDERSSON, Rolf; Akzo Nobel Surface Chemistry AB, S-444 85 Stenungsund (SE).</p>		<p>(81) Designated States: AU, BR, CA, CN, ID, IN, JP, MX, PL, RU, SG, TR, US, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: NONIONIC CELLULOSE ETHER WITH IMPROVED THICKENING PROPERTIES</p> $\text{RO}-(\text{C}_2\text{H}_4\text{O})_n\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2- \quad (I)$ <p>(57) Abstract</p> <p>The present invention relates to associative cellulose ethers with improved thickening effects, especially in paint. The improvement depends on the presence of a hydrophobic modifying group of general formula (I), where R is an aliphatic group of 12–22 carbon atoms and n is a number from 3 to 7. The DS of the hydrophobic group is 0.003–0.012.</p>		

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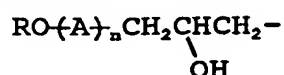
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NONIONIC CELLULOSE ETHER WITH IMPROVED THICKENING PROPERTIES

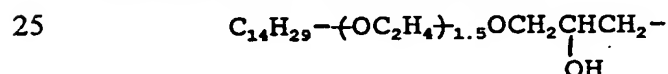
This invention relates to new nonionic cellulose ethers with improved thickening effects, especially in paint compositions. The improvements depend on the presence of hydrophobic substituents having a poly(oxyethylene) spacer between a large aliphatic group and the linkage to the cellulose ether.

The US Patent 4 228 277 discloses associative water-soluble nonionic cellulose ethers of the so called associative type. They contain as a modifying substituent a C₁₀ to C₂₄ long chain alkyl group which may be introduced by reacting a water-soluble cellulose ether and a suitable amount of the corresponding C₁₀ to C₂₄ epoxide.

In EP-A-390 240 associative nonionic cellulose ethers are described which may contain hydrophobic substituents of the formula

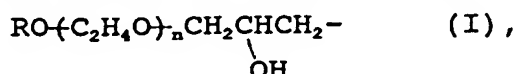


where R is a hydrophobic group containing 8-36 carbon atoms, A is an alkyleneoxy group having 2-3 carbon atoms and n is a number from 0 to 6. In Example F the publication discloses an ethyl hydroxyethyl cellulose ether containing the hydrophobic substituent



The degree of substitution of this group was 0.016.

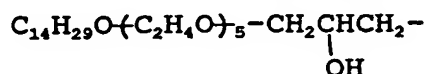
It has now been found that the properties of the prior art nonionic cellulose ethers are further improved by introducing into the nonionic cellulose ether a hydrophobic modifying group of the general formula



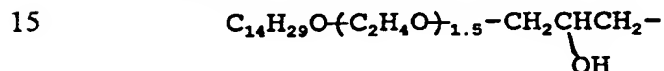
where R is an aliphatic group of 12-22 carbon atoms and n is a number from 3 to 7 with a degree of substitution of 0.003-0.012. The hydrophobically modified cellulose ether may have a viscosity of 20-15000 mPa's, suitably 100-12000 mPa's, and

preferably 150-4000 mPa's, measured in a 1% by weight water solution with a StressTech rheometer from Rheologica, equipped with a 4 cm 1° cone and plate system, at 20°C ± 0.1°C. The rheometer was put in the constant shear mode and all the viscosities were measured at the newtonian plateau, characterized by a shear rate independent viscosity.

Extensive studies have shown that the length of the spacer, that is to say the length of the hydrophilic group $\text{(C}_2\text{H}_4\text{O)}_n$ positively affects the thickening, levelling and high shear viscosity in paint compositions. For example, the contribution of the thickening effect of the group



is higher than the effect of the group



Very surprising is also the fact that the thickening effect of the long spacer is more pronounced the larger the aliphatic group is. Preferably R is an aliphatic group of 14-20 carbon atoms and n is a number from 3 to 5. Even if larger aliphatic groups and higher values of n will further improve the viscosity, such high viscosities will normally not be required.

Besides the hydrophobic group the cellulose ether may contain lower alkyl substituents such as methyl, ethyl or propyl, or hydroxyalkyl substituents as hydroxyethyl, hydroxypropyl or hydroxybutyl or combinations thereof. The substituent and the degree of substitution are chosen so that the associative cellulose ethers of the invention become water-soluble or water-dispersable.

It has also been found that cellulose ethers, substituted with a group of the formula I and having a low degree of polymerisation, have remarkably favourable properties. These cellulose ethers have a unique combination of high associative thickening effect, high hydrophilicity and a comparatively low thickening effect depending on the

length of the cellulose chain. The unique combination of properties depends on the fact that the hydrophilicity of the large spacer of the group I increases the hydrophilicity of the cellulose ether and at the same time the associative
 5 thickening effect of the group I. The unique properties of these cellulose ethers can for example be utilized to improve the levelling, sagging and spatter of paint compositions.

The differences in DP between cellulose ethers may
 10 easily be measured by determining the "DP viscosity" in a blend of diethylene glycol monobutylether and water in a weight ratio of 20:80. In such a blend all hydrophobic associations are broken and the viscosity depends on the length of the cellulose chain. In this context the DP
 15 viscosity means the viscosity of 1% by weight of cellulose ether dissolved in the blend divided by 2.7. The DP viscosity value indicates an average DP value of the cellulose ether. According to the invention the cellulose ethers normally have a DP viscosity of 15-200 mPa's. In
 20 paint compositions the DP viscosity of the cellulose ethers are preferably 20-100 mPa's.

The cellulose ethers of the invention may be prepared by using known process steps. For example an alkali cellulose and suitable reactants can be reacted in the presence
 25 of an alkaline catalyst in order to introduce low alkyl groups and/or hydroxyalkyl groups in such amounts that the intermediate cellulose ethers obtained are water soluble. This intermediate cellulose ether product and a reactant having the formula



in which R and n have the meaning mentioned above, are then reacted at an elevated temperature and in the presence of an alkaline catalyst to form a cellulose ether according to the
 35 invention.

Suitable water-soluble ethers to which the

hydrophobic group is added are alkyl cellulose, alkyl hydroxyalkyl cellulose and hydroxyalkyl cellulose. Specific examples of such cellulose ethers include methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, 5 hydroxyethyl cellulose, methyl cellulose, hydroxyethyl hydroxypropyl cellulose, ethyl hydroxyethyl cellulose, methyl ethyl hydroxyethyl cellulose and methyl hydroxyethyl hydroxypropyl cellulose. Preferred cellulose ethers are alkyl hydroxyalkyl celluloses, such as methyl hydroxyethyl 10 cellulose, methyl ethyl hydroxyethyl cellulose and ethyl hydroxyethyl cellulose; and hydroxyethyl cellulose.

The hydrophobically modified cellulose ethers of the invention may advantageously be used as a colloid stabilizer, thickener or reology modifier. Typical 15 application areas are aqueous paint formulations, such as latex paints; cosmetics, such as shampoos and conditioners; detergent compositions, such as surface cleaners and compositions for laundry; and paper coating compositions.

The cellulose ethers may advantageously be used in 20 water-based flat, semi-flat and semi-gloss paints. The amounts added of the cellulose ethers vary depending on both the composition of the paints and the substitution and viscosity of the cellulose ethers, but normally the addition is 0.2-1% by weight of the paints. Suitable binders are 25 emulsion binders, such as alkyd resins, and latex binders, such as polyvinyl acetate, copolymers of vinyl acetate and acrylate, copolymers of vinyl acetate and ethylene, copolymers of vinyl acetate, ethylene and vinyl chloride and copolymers of styrene and acrylate. The latex binders are 30 often stabilized with anionic surfactants.

The present cellulose ethers are much more versatile thickeners than earlier known associative nonionic cellulose ethers. The paint formulator has the possibility to affect the final paint properties to a very high extent. The 35 present cellulose ethers can be used in all types of paints ranging from low to high PVC, and for interior as well as exterior use. They contribute to the following paint

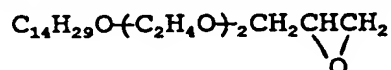
properties:

- low spatter
- good film build
- good flow and levelling
- low sag

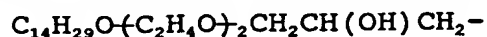
The present invention and the advantages of the present cellulose ethers are further illustrated by the following examples.

Example A

- One mole of tetradecanol ethoxylated with 2 moles of ethylene oxide per mole of tetradecanol and one mole of epichlorohydrin were reacted in the presence of tin tetrachloride at a temperature of 60 to 70°C and a glycidyl ether was obtained. A solution of 30% sodium hydroxide in water was added at 80°C. After 30 minutes under vigorous stirring at 80°C, the resulting glycidyl ether was separated from the water phase. It had the structure



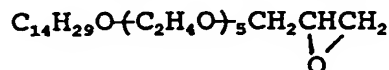
- Powder of dissolving wood pulp was added to a reactor. After evacuation of the air, 0.7 g of sodium hydroxide (50%w/w in water) were first added per gram of wood pulp followed by addition of 0.84 g of ethylene oxide, 1.5 g of ethyl chloride and 0.040 g of the glycidyl ether calculated on one gram of wood pulp. After the additions the temperature in the reactor was increased to 55°C and held there for 50 minutes. The temperature was then increased to 105°C and maintained for 50 minutes. The cellulose ether obtained was washed with boiling water and neutralised with acetic acid. The cellulose ether had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.008$, where R is the group



Example B

- Example A was repeated but the tetradecanol ethoxylate had 5 moles of ethylene oxide per mole of tetradecanol. The

tetradecanol ethoxylate and epichlorohydrin were reacted and a glycidyl ether of the formula

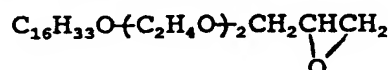


5 was obtained. In the production of the cellulose ether the amount of glycidyl ether was 0.055 g per g of wood pulp. The cellulose ether obtained had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.007$, where R is the group

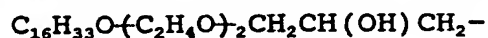


10 Example C

Example A was repeated but a hexadecanol ethoxylate with 2 moles of ethylene oxide per mole of hexadecanol was used instead of the tetradecanol ethoxylate. The hexadecanol ethoxylate and epichlorohydrin were reacted and a glycidyl
15 ether of the formula

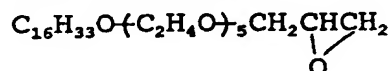


was obtained. In the production of the cellulose ether the amount of glycidyl ether was 0.042 g per g of wood pulp. The
20 cellulose ether obtained had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.008$, where R is the group



Example D

Example B was repeated but hexadecanol ethoxylate with 5
25 moles of ethylene oxide per mole of hexadecanol was used instead of the tetradecanol ethoxylate. The hexadecanol ethoxylate and epichlorohydrin were reacted and a glycidyl ether of the formula



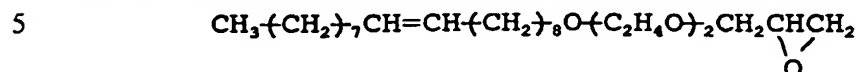
30 was obtained. In the production of the cellulose ether the amount of glycidyl ether was 0.058 g per g of wood pulp. The cellulose ether obtained had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.008$, where R is the group



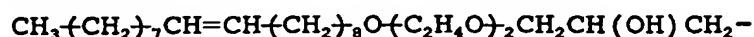
Example E

Example A was repeated but an oleylalcohol ethoxylate with 2

moles of ethylene oxide per mole of oleylalcohol was used instead of the tetradecanol ethoxylate. The oleylalcohol ethoxylate and epichlorohydrin were reacted and a glycidyl ether of the formula

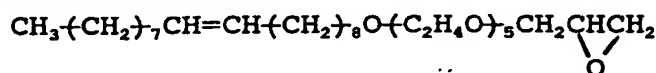


was obtained. In the production of the cellulose ether the amount of glycidyl ether was 0.053 g per g of wood pulp. The cellulose ether obtained had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.008$, where R is the group

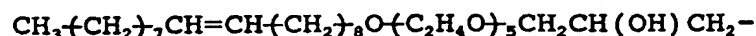


Example F

Example B was repeated but an oleylalcohol ethoxylate with 5 moles of ethylene oxide per mole of oleylalcohol was used instead of the tetradecanol ethoxylate. The oleylalcohol ethoxylate and epichlorohydrin were reacted and a glycidyl ether of the formula

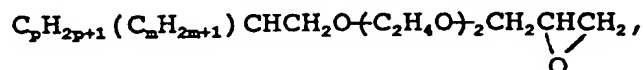


was obtained. In the production of the cellulose ether the amount of glycidyl ether was 0.065 g per g of wood pulp. The cellulose ether obtained had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.008$, where R is the group



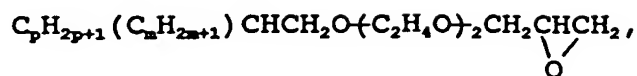
25 Example G

Example B was repeated but an adduct mixture of 2-octyldecanol, 2-hexyldodecanol, 2-octyldodecanol, 2-hexyldecanol and 2 moles of ethylene oxide per mole of the alcohol mixture was used instead of the tetradecanol ethoxylate. The adduct mixture and epichlorohydrin were reacted and a glycidyl ether of the formula



where p is 6-8 and m is 8-10, was obtained. In the production of the cellulose ether the amount of glycidyl ether was 0.047 g per g of wood pulp. The cellulose ether obtained had a $\text{MS}_{\text{hydroxyethyl}}=2.1$, a $\text{DS}_{\text{ethyl}}=0.8$, and a $\text{DS}_R=0.006$,

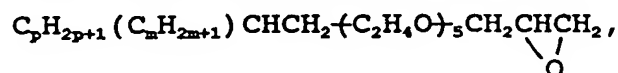
where R is the group



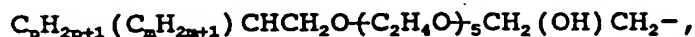
where p and m have meanings mentioned above.

5 Example H

Example B was repeated but an adduct mixture of 2-octyldecanol, 2-hexyldodecanol, 2-octyldodecanol, 2-hexyldecanol and 5 moles of ethylene oxide per mole of the alcohol mixture was used instead of the tetradecanol
10 ethoxylate. The adduct mixture and epichlorohydrin were reacted and a glycidyl ether of the formula



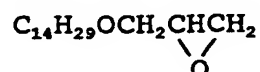
where p is 6-8 and m is 8-10, was obtained. In the
15 production of the cellulose ether the amount of glycidyl ether was 0.065 g per g of wood pulp. The cellulose ether obtained had a $MS_{hydroxyethyl}=2.1$, a $DS_{ethyl}=0.8$, and a $DS_R=0.004$, where R is the group



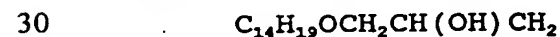
20 where p and m have meanings mentioned above.

Example I

Example A was repeated but tetradecanol and epichlorohydrin were directly reacted and a glycidyl ether of the formula



25 was obtained. In the production of the cellulose ether the amount of the glycidyl ether was 0,029 g per g of wood pulp. The cellulose ether obtained had a $MS_{hydroxyethyl}=2.1$, a $DS_{ethyl}=0.8$, and a $DS_R=0.09$, where R is the group



Example 1

A cellulose ether solution containing 1% by weight of any one of the cellulose ethers in Examples A-I in deionised and distilled water were prepared. The viscosities of the
35 solutions were measured with a StressTech rheometer from Rheologica, equipped with a 4 cm 1° cone and plate system,

at 20°C ± 0.1°C. The rheometer was put in the constant shear mode and all the viscosities were measured at the newtonian plateau, characterized by a shear rate independent viscosity. The following results were obtained.

5

Test No	Cellulose ether				Viscosity mPa.s	DP Viscosity mPa.s
	Example	Alipatic group	n	DS _R		
1	A	C ₁₄ H ₂₉ -	2	0.008	1660	47
2	B	C ₁₄ H ₂₉ -	5	0.007	2851	52
3	C	C ₁₆ H ₃₃ -	2	0.008	561	55
4	D	C ₁₆ H ₃₃ -	5	0.008	721	54
5	E	Oleyl	2	0.008	3172	54
6	F	Oleyl	5	0.008	4415	54
7	G	(1)	2	0.006	2333	41
8	H	(1)	5	0.004	2565	46
9	I	C ₁₄ H ₂₉ -	0	0.009	1300	92

(1) = C_pH_{2p+1}(C_mH_{2m+1})CHCH₂-, where p is 6-8 and m is 8-10.

From the results it is evident that the thickening efficiency of the cellulose ethers increases with the length of the spacers. The low viscosities of the water solution of the cellulose ethers C and D depend on the fact that phase separation occurs at 20°C.

Example 2

Semi-gloss latex paints were prepared and one of the cellulose ethers in examples A-I was added in such an amount that a latex paint of a Stormer viscosity of 110 KU was obtained.

The latex paints had the following composition.

10

	Ingredient	Parts by weight
	Water	243.5 - x
	Cellulose ether	x
	Bactericide	1
5	Dispersing agent	6,5
	Defoamer	5
	Titanium dioxide	180
	Calcium carbonate	110
	Latex (Vinamul 3650)	454

10

The amounts of cellulose ether needed to obtain a Stormer viscosity of 110 were as follows.

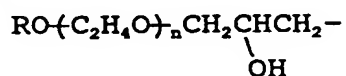
Test No	Cellulose ether Example	Spacer n	Amount parts by weight
10	A	2	4.0
11	B	5	3.5
12	C	2	4.1
13	D	5	3.7
14	E	2	3.0
15	F	5	2.8
16	G	2	4.0
17	H	5	3.5
18	I	0	4.0

- 15 From the results it is evident that the cellulose ethers with the longer ethylene oxide spacer (Tests 11, 13, 15 and 17) give a latex paint with a Stormer viscosity of 110 KU at a lower amount of addition than the cellulose ethers with shorter spacers. In the paint formulation the cellulose
- 20 ethers of Examples C and D do not cause any phase

separations.

C L A I M S

1. A nonionic associative cellulose ether, characterized in that it contains a modifying hydrophobic group of the formula



where R is an aliphatic group of 12-22 carbon atoms and n is a number from 3 to 7, with a degree of substitution of 0.003-0.012.

2. A cellulose ether according to claim 1, characterized in that it has a viscosity of 20-15000 mPa's measured in a 1% water solution at 20°C.
3. A cellulose ether according to claims 1 or 2, characterized in that it has a DP viscosity of 15-200 mPa's.
4. A cellulose ether according to claim 3, characterized in that the degree of substitution is from 0.003 to 0.012.
5. A cellulose ether according to any one of claims 1 to 4, characterized in that the cellulose ether is a modified water-soluble alkyl cellulose, hydroxyalkyl cellulose or alkyl hydroxyalkyl cellulose.
6. A cellulose ether according to claim 5, characterized in that the cellulose ether is a modified methyl hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, methyl ethyl hydroxyethyl cellulose or hydroxyethyl cellulose.
7. A cellulose ether according to any one of claims 1 to 6, characterized in that it has a DP viscosity of 20-100 mPa's.
8. A cellulose ether according to any one of claims 1 to 7, characterized in that it has a viscosity of 100-12000 mPa's measured in 1% water solution at 20°C.
9. A paint composition characterized in that it comprises a film forming latex and an aqueous phase thickened with a nonionic cellulose ether according to any one of claims 1-8.
10. Use of the cellulose ethers in any one of claims 1-9

as a colloid stabilizer, thickener or reology modifier.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/01291

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08B 11/193, C09D 7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08B, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5140099 A (PETER BOSTRÖM ET AL), 18 August 1992 (18.08.92) --	1-10
A	EP 0390240 A1 (BEROL NOBEL AB), 3 October 1990 (03.10.90) --	1-10
A	US 4228277 A (LEO M. LANDOLL), 14 October 1980 (14.10.80) -- -----	1-10

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PCT/SE 99/01291

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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